

Use of Acrylates Copolymer as Waterproofing Agent in Personal Care Applications

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BACKGROUND OF THE INVENTION

The present invention relates to the use of acrylate copolymers as water proofing agents in personal care products.

10 Many personal care products rely on water proofing agents for their overall functionality. For example, there is a consumer need for mascaras, which will not come off upon crying, and sunscreen lotions which will not come off during swimming. Although there exist many personal care products which claim water resistance or water proofing, there is a need for longer lasting water resistance with improved aesthetics. Many existing products that claim water resistance are waxy, greasy or heavy in feel, making them
15 undesirable to consumers. Further, many of the agents currently used in personal care products to impart water resistance are difficult to handle or incorporate into the formulations.

A poly(vinylpyrrolidone/eicosene) copolymer currently used in many personal care formulations to impart water proofing, is oil soluble, and results in a formulation with an
20 unpleasant greasy, waxy or heavy afterfeel. Further, it is difficult to incorporate into products in that it cannot just be mixed in at any point during processing. This poly(vinylpyrrolidone/eicosene) copolymer may also increase the formulation viscosity dramatically, resulting in difficulties in formulating products with desired properties.

Consumers are demanding not only improved water resistance of their personal
25 care products, but also smooth, creamy formulations, which are neither waxy nor heavy and greasy in feel. Manufacturers are demanding that such water proofing agents be easy to incorporate into products, particularly in the aqueous phase, without the need for heat, neutralization, or other special processing, thus allowing greater formulation versatility.

30 Surprisingly, it has now been found that the use of acrylate copolymers provide excellent water resistance to personal care products without the undesirable waxy, greasy or heavy feel. Further, these acrylate copolymers are easy for manufacturers to use as they can be easily incorporated into the water phase without special processing.

SUMMARY OF THE INVENTION

The present invention relates to the use of acrylate copolymers, which provide excellent water resistance to personal care products without the undesirable waxy, greasy or heavy feel. Further, these acrylate copolymers are easy for manufacturers to use as they can be easily incorporated into the water phase without special processing.

Acrylate copolymers, as used herein, is intended to mean polymers consisting of at least two acrylate monomers, which will result in a copolymer that is water dispersible.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the use of acrylate copolymers, which provide excellent water resistance to personal care products and are easy for manufacturers to use as they can be easily incorporated into the water phase without special processing. Further, these acrylates copolymers do not give undesirable greasy, waxy or heavy skin feel.

The acrylate copolymer is a polymer formed from at least two monomers selected from acrylic and methacrylic acids, and esters and/or amides of acrylic acid or methacrylic acid and is intended to include in particular methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, isobutyl(meth)acrylate, hydroxypropyl methacrylate, and hydroxyethyl methacrylate. Particularly suitable monomers are butyl acrylate, methylmethacrylate, and methacrylic acid. Such acrylate polymers are water dispersible and exclude those having more than trace amounts of hydrophobic monomers which contain an alkyl group of greater than or equal to C6, more particularly C8. Most particularly suitable acrylate polymers are those with a net anionic charge at a pH of above about 4, though one skilled in the art would understand that this net anionic charge would increase as the pH increases.

In a particularly suitable embodiment, the acrylate copolymer contains about 1 to 85% butyl acrylate, about 1 to 87% methylmethacrylate, and about 1 to 25% methacrylic acid, by weight. In a more particularly suitable embodiment, the acrylate copolymer contains about 38 to 48% butyl acrylate, about 39 to 49% methylmethacrylate, and about 8 to 18% methacrylic acid, by weight.

The acrylate copolymer is typically provided in the form of an emulsion which is a thin, non-viscous liquid as a 45% polymer-in-water emulsion. The acrylate copolymer may also be provided in a dry form.

The acrylate copolymer may be used in any amount necessary to achieve the desired functionality and properties of the personal care products. Typically, it will present

in an amount of from about 0.2 to 10%, particularly in an amount of about 0.5 to 4%, more particularly about 1 to 2%, by weight of the personal care composition.

5 The acrylate copolymer may be added to the personal care composition at any feasible point in the process. In an emulsion formula, the acrylates copolymer can be added to the aqueous phase prior to emulsification, during the emulsification or heating stage, during the cool down stage, or after cool down. The acrylate copolymer is dispersible in cold (room temperature) water without the need for added heat. Further, there is no need to neutralize the polymer or apply any other special processing to achieve sufficient dispersion in water or other aqueous media.

10 Neutralization is not only unnecessary, but no substantial neutralization is particularly suitable for the acrylate copolymers of this invention. When neutralization is carried out, it is done using bases and methods known in the art, and is preferably not to the point of complete polymer neutralization resulting in polymer solubilization. However, it is understood that this invention includes those embodiments in which the acrylate copolymers are neutralized, even 100% neutralized.

15 The personal care composition or product can be any desired by the consumer for use on the skin, eyelashes or eyebrows, including without limitation, cosmetic compositions such as mascara, facial foundations, eyeliners, lipsticks, and color products; skin care compositions such as moisturizing lotions and creams, skin treatment products, skin protection products in the form of an emulsion, liquid, stick, or a gel; sun care compositions such as sunscreens, sunscreen emulsions, lotions, creams, sunscreen emulsion sprays, liquid/alcohol sunscreen sprays, sunscreen aqueous gels, broad spectrum sunscreens with UVA and UVB actives, sunscreens with organic and inorganic actives, sunscreens with combinations of organic and inorganic actives, suntan products, self-tanning products, and after sun products etc. Particularly suitable compositions are personal care emulsions, more particularly suitable are sun care compositions such as sunscreen emulsions and sunscreen emulsion sprays. The personal care composition may be in any form, including without limitation in sprays, emulsions, lotions, gels, liquids, sticks, waxes, pastes, powders, and creams.

25 The personal care composition will contain other components commonly used in the industry, and these will vary greatly depending upon the type of composition and the functionality and properties desired. Without limitation, these components include thickeners, suspending agents, emulsifiers, UV filters, sunscreen actives, humectants, moisturizers, emollients, oils, waxes, solvents, chelating agents, vitamins, antioxidants, botanical extracts, silicones, neutralizing agents, preservatives, fragrances, dyes,

pigments, conditioners, polymers, antiperspirant active ingredients, anti-acne agents, anti-dandruff actives, surfactants, exfoliants, film formers, propellants, tanning accelerator, hair fixatives and colors. The acrylate copolymers of the present invention are compatible with most other components used in conventional personal care compositions. For example, 5 sunscreen compositions may contain at least one component selected from the group comprising organic UV filters, inorganic UV actives, UVA and/or UVB sunscreen actives, octinoxate, octisalate, oxybenzone, homosalate, octocrylene, avobenzene, titanium dioxide, starch, conditioning agents, emulsifiers, rheology modifiers and thickeners, neutralizers, emollients, solvents, film formers, moisturizers, antioxidants, vitamins, 10 chelating agents, preservatives, fragrances, and zinc oxide. Skin care and cosmetic compositions may contain at least one component selected from the group consisting of vitamins, anti-aging agents, moisturizers, emollients, emulsifiers, surfactants, preservatives, pigments, dyes, colors and insect repellents.

The resultant personal care compositions are water resistant. Using the test 15 described in the example section below, the acrylate copolymers of this invention are water resistant for at least 40 minutes, more particularly at least 60 minutes, most particularly at least 80 minutes. The SPF retention provided by the polymer in a sunscreen is more than 60%, preferably more than 80%, and more preferably more than 90% after 80 minutes immersion in water. Sunscreens with the polymer have shown higher SPF 20 value comparing with the same sunscreen base without polymer, particularly after immersion in water.

The resultant personal care compositions have excellent feel on the skin, exhibiting no noticeable waxiness, greasiness or heavy feeling. Further, the compositions have excellent rub-off resistance, film forming properties, and moisturizing effects. 25

EXAMPLES

The following examples are presented to further illustrate and explain the present invention and should not be taken as limiting in any regard. All percents used are on a weight basis. 30

The following ingredient is used in the examples:
Dermacryl® AQF polymer, Acrylates Copolymer, 45% active polymer-in-water emulsion (commercially available from National Starch and Chemical Company, Bridgewater, NJ, USA) 35

Example 1 – Water resistant Sunscreen Cream

Ingredient	INCI Designation	% W/W	
		Blank	Formula1
Phase A			
D.I. water	Water	48.90	44.50
Pricerine 9088	Glycerine 99.5%	5.00	5.00
Carbopol 940(2%)	Carbomer	10.00	10.00
Pemulen TR-2	Acrylates/C10-30 Alkyl Acrylate Cross Polymer	0.20	0.20
Phenonip	Phenoxyethanol and Methyl Paraben and Butyl Paraben and Ethyl Paraben and Propyl Paraben	1.00	1.00
TEA 99%	Triethanolamine	0.40	0.40
Dermacryl AQF (45% active) polymer	Acrylates Copolymer	0.00	4.40
Phase B			
Neo Heliopan AV	Ethylhexyl Methoxycinnamate	7.50	7.50
Neo Heliopan BB	Benzophenone-3	6.00	6.00
Neo-Heliopan OS	Ethylhexyl Salicylate	4.00	4.00
Uvinul M-539T	Octocrylene	9.00	9.00
Protachem GMS-450	Glyceryl Stearate	2.50	2.50
Pristerine 4911	Stearic Acid	2.50	2.50
Prisorine 3515	Isostearyl Alcohol	1.00	1.00
Amphisol	DEA-Cetyl Phosphate	2.00	2.00
Total		100.00	100.00
Viscosity* (cps)		76.000	84.000

* Viscosity was measured using Brookfield DV-I, spindle #6 at 10 rpm, 23°C

- Mixing procedure: Water and glycerine were combined at room temperature with propeller mixing, Carbopol 940 and Pemulen TR-2 were dispersed in the water/glycerin mixture and mixed until smooth. The rest of the phase A ingredients were then added in order while stirring. Phase A and B were heated separately to 70-75°C with propeller mixing. When both phase A and phase B reached temperature, B was added to A with vigorous mixing. The temperature was kept at 75°C for an additional 15 minutes, then the heat was dispersed and cooling was started with moderate mixing until ambient temperature was reached.

Example 2 - Water Resistant Sunscreen Spray Lotion

Ingredient	INCI name	%w/w
Phase A		Formula 2
Neo Heliopan OS	Ethylhexyl Salicylate	5.00
Escalol 567	Benzophenone-3	3.00
Homosalate	Homosalate	7.00
Neo Heliopan AV	Ethylhexyl Methoxycinnamate	7.50
Finsolv TN	C12-15 Alkyl Benzoate	5.00
Stearyl Alcohol	Stearyl Alcohol	1.50
Phase B		
D.I. Water	Water	62.00
Versene NA	Disodium EDTA	0.10
Arlatone V-100	Steareth-100 (and) Steareth-2 (and) Glyceryl Stearate Citrate (and) Sucrose (and) Mannan (and) Xanthan Gum	1.50
Pricerine 9088	Glycerine 99.5%	2.00
Dermacryl AQF (45% active) polymer	Acrylates Copolymer	4.40
Phase C		
Phenonip	Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	1.00

Mixing Procedure: Arlatone V-100 was dispersed in cold water until homogeneous. The remaining ingredients of the phase B were mixed in and heated to 75-80°C. Phase A was
5 mixed in and heated to 75-80°C. Phase A was slowly added to phase B while stirring with high speed and then stirred for 10 minutes. The mixture was homogenized for 2 minutes. And Part C was added and mixed until uniform.

Example 3 – Water Resistant Sunscreen Emulsion Spray

	%w/w			
Ingredient	Formula 3	Formula 4	Formula 5	Formula 6
Phase A				
D.I. Water	74.11	78.51	74.26	76.51
Disodium EDTA	0.04	0.04	0.04	0.04
Pemulen TR-1	0.20	0.20	0.20	0.20
Glycerin 99.5%	3.00	3.00	3.00	3.00
Phenonip	1.00	1.00	1.00	1.00
Dermacryl AQF (45% active) polymer	4.40	0.00	0.00	0.00
Phase B				
Ethylhexyl Methoxycinnamate	7.50	7.50	7.50	7.50
Ethylhexyl Salicylate	5.00	5.00	5.00	5.00
Benzophenone-3	4.00	4.00	4.00	4.00
Cetearyl Alcohol	0.30	0.30	0.30	0.30
Sorbitan Oleate	0.45	0.45	0.45	0.45
PVP/ Eicosene Copolymer	0.00	0.00	0.00	2.00
Phase C				
Acrylates/C12-22 Alkylmethacrylate Copolymer	0.00	0.00	4.25	0.00
Phase D				
Triethanolamine	q.s. to pH 6.5	q.s. to pH 6.5	q.s. to pH 6.5	q.s. to pH 6.5
Total	100.00	100.00	100.00	100.00

- 5 Mixing procedure: Phase A and B were combined separately and heated to 75°C with mixing. Phase B was added to A with vigorous mixing and mixed at 75°C for 15 minutes. Cooling was then started and continued until the temperature dropped below 40°C. Phase C was added (for Formula 5 only) and mixed thoroughly. Phase D was added to adjust pH at the end.

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Viscosity (Brookfield DV-I, spindle #6@10rpm, measured at 23°C):

- Formula 3 (Dermacryl AQF polymer): 4200cps
 Formula 4 (Blank) : 5800cps
 15 Formula 5 (Acrylates/C12-22 Alkylmethacrylate Copolymer): 9100cps
 Formula 6 (PVP/ Eicosene Copolymer): 12100cps

- The resultant sunscreen spray emulsion has no significant viscosity increase by addition of Dermacryl AQF polymer, and the formula has excellent spray patterns. The formula with Dermacryl AQF polymer was similar in viscosity to the base with no polymer and less viscous than a similar formula with Acrylates/C12-22 Alkylmethacrylate Copolymer or PVP/ Eicosene Copolymer. The formula with Dermacryl AQF polymer has excellent spray aesthetics and less particle drift resulting in more uniform coverage.

Example 4 - Broad Spectrum Water Resistant Sunscreen Lotion

Ingredient	INCI name	%w/w
Phase A		Formula 7
Deionized water		47.70
Disodium EDTA		0.10
Carbopol 940(2% solution)	Carbomer	15.00
Propylene glycol		2.00
Dermacryl AQF (45% active) polymer		4.40
Phase B		
Corapan TQ	Diethylhexyl naphthalate	5.00
Parsol 1789	Avobenzene	3.00
Neo Heliopan BB	Benzophenone-3	4.00
Neo Heliopan OS	Octyl salicylate	5.00
Neo Heliopan HMS	Homosalate	5.00
Finsolv TN	C12-15 alkyl benzoate	5.00
Brij 721	Steareth-21	1.00
Brij 72	Steareth-2	0.80
Protachem GMS-450	Glyceryl stearate	1.00
Phase C		
Triethanolamine		q.s. to pH 6.5
Phase D		
Phenonip		1.00

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Mixing procedure: Phase A ingredients were combined at room temperature with moderate propeller mixing. Phase A was then heated to 75°C. Phase B ingredients were combined and heated 75°C with propeller mixing. When both Phase A and B reached temperature, B was added to A with vigorous propeller mixing. The mixture was then cooled to below 40°C with moderate propeller mixing, the pH was adjusted with TEA, and Phenonip was added and mixed until uniform.

Example 5 - Water Resistant Sunscreen with ZnO

Ingredient	INCI name	%w/w
Phase A		Formula 8
Arlacel 165	Glyceryl stearate (and) PEG-100 stearate	3.50
Montanov S	Cocoglucoside (and) coconut alcohol	1.30
	Isodecyl neopentanoate	8.00
Neo Heliopan OS	Ethylhexyl salicylate	5.00
Escalol 567	Benzophenone-3	3.00
Neo Heliopan AV	Ethylhexyl methoxycinnamate	7.50
Zinc oxide neutral	Zinc oxide	7.00
Dow 345	Cyclomethicone	5.00
Phase B		
Keltrol CGT	Xanthan Gum	0.25
Veegum Ultra	Magnesium aluminum silicate	1.50
D.I. Water	Water	52.35
Tetrasodium EDTA		0.20
Dermacryl AQF (45% active) polymer		4.40
Phase C		
Phenonip		1.00

Mixing Procedure: All ingredients in Phase A were combined, except Zinc oxide and Dow 345, and heated to 75-80°C. Zinc oxide was dispersed into the above portion of Phase A. Phase B was combined and all solid ingredients were dispersed in water completely. Phase B was heated to 75°C. When both Phase A and B reached temperature, A was added to B and homogenized for 5 minutes. Cooling was started with continuously mixing. Dow 345 was added at 65°C and homogenized for 5 minutes more. The mixture was cooled with moderate stirring and Phase C was added when the temperature dropped below 40°C.

Example 6 – Water Resistant Sunscreen with TiO₂

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Ingredient	INCI name	%w/w
Phase A		Formula 9
D.I. water	Water	50.40
Disodium EDTA		0.10
Phenonip		1.00
1,2 Propanediol	Propylene glycol	3.00
Keltrol CG-RD	Xanthan gum	0.35
CMC 7LF	Cellulose Gum	0.05
Dermacryl AQF (45% active) polymer		4.40

Phase B

Neo Heliopan AV	Ethylhexyl methoxycinnamate	7.50
Neo Heliopan BB	Benzophenone-3	2.00
MT-500B-MS5	TiO ₂ + methicone	11.00
Myritol 318	Caprylic/capric triglyceride	9.00
DC 345	Cyclomethicone	3.50
Finsolv TN	C12-15 alkyl benzoate	1.50
Vitamin E acetate	Tocopheryl acetate	0.20
Amphisol	DEA-cetyl phosphate	2.50
Brij 72	Steareth-2	1.85
Brij 721	Steareth-21	0.65
Protachem GMS-450	Glyceryl stearate	1.00

Mixing procedure: Phase A ingredients were combined at room temperature with moderate propeller mixing. After making sure that the gums were well dispersed, heating was started to 70-75°C. Phase B ingredients were combined and mixed vigorously for 20 minutes, allowing for a good dispersion of TiO₂. Phase B was heated to 75-80°C with
5 propeller mixing. When both Phase A and B reached temperature, B was added to A with vigorous propeller mixing. The temperature was kept at 75°C for an additional 15-20 minutes while mixing thoroughly. Phase C was then added, mixed and cooled to ambient temperature.

Example 7 – In-Vivo Very Water Resistant Sunscreen Test Results

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A 5 subject panel was tested per the FDA final monograph ("Sunscreen Drug Products for Over-The-Counter Human Drugs," Rule, 21 CFR Part 352, Subpart D (Federal Register/ Vol. 64, No. 98/ Friday May 21, 1999, Proposed Amendment; Docket number 78N-0038/CP12, June 21, 1999) for very water resistant sunscreens. A formula containing
15 DERMACRYL AQF film forming polymer was compared with the base formula containing no polymer (blank). The formulas were evaluated after an 80 minute immersion in water. The results are described below (Table 1).

Table 1: In-Vivo Test Results

	Blank	Formula 1
	no polymer	DERMACRYL AQF
Static	32	32
Post Immersion	<21	31
Standard Deviation	0	1.15

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Example 8 – In-Vitro Very Water Resistant Sunscreen Test Results

The In-Vitro sunscreen waterproof/water resistance test method: Vitro-Skin N-19 (available from IMS Inc.) was used as the substrate for this test. Labsphere UV 1000S ultraviolet transmittance analyzer was used to measure the SPF values. Vitro-skin had been hydrated prior to use in a hydration chamber with humidity regulated by the solution of water/glycerin at 23°C for 16 hours. Sunscreen was then applied onto the hydrated vitro-skin (6.2cmx9.0cm each piece), with the product dose of 2ul/cm². Initial SPF value was then measured, followed by immersing the samples in water bath, and setting the stirring motor to 300rpm. For waterproof or very water resistance test, the samples were immersed in water for 80 minutes. The SPF after water immersion was then measured after excess water had been removed from the samples and after the samples were equilibrated in the chamber for 2 hours. Each test sample was run in triplicate, and each vitro-skin was scanned 10 times when SPF was measured.

Formulation	SPF (after 80 min in H2O)	% SPF Retention after immersion*	SPF value enhancement over blank** (after 80 min in H2O)
Formula 2	30.2 (0.9)***	100%	25.6
Formula 3	33.5 (1.1)	100%	15.6
Formula 7	37.3 (2.2)	86%	32.5
Formula 8	51.9 (0.8)	100%	41.6

* % SPF Retention after immersion

= SPF (after 80 minutes in water)/SPF (initial, before 80 minutes in water)

** SPF value enhancement over blank

= SPF (formula with Dermacryl AQF polymer) – SPF (same formula without Dermacryl AQF polymer)

*** Standard Deviation

Example 9 – Sunscreen Aqueous Gel containing Dermacryl AQF- Cold Process

Ingredient	INCI name	%w/w
Phase A		Formula 10
Neo Heliopan Hydro	Phenylbenzimidazole Sulfonic Acid	5.00
Deionized water		10.0
TEA 99%	Triethanolamine	5.5
Phase B		
D.I. Water	Water	q.s.
Disodium EDTA		0.10
Structure XL	Hydroxypropyl Starch Phosphate	5.0
Escalol 587	Benzophenone-4	3.0
Dermacryl AQF (45% active) polymer	Acrylates Copolymer	4.40
Phase C		
Germaben II		1.00

- 5 Mixing Procedure: Neo Heliopan Hydro and the water were preheated. Triethanolamine was added and mixed well. The ingredients of phase B were then combined in order and mixed until homogeneous. Phase A was added to B and mixed until homogeneous. Phase C was added to the batch with mixing.

Example 10 – Face Foundation

Ingredient	INCI name	%w/w
Phase A		Formula 11
D.I. water	Water	q.s.
Polyglycol E-400	PEG-8	5.0
1,2 Propanediol	Propylene glycol	5.0
Dermacryl AQF (45% active) polymer	Acrylates copolymer	4.40
Phase B		
Ceraphyl 140A	Decyl oleate	2.2
Cerasynt Q	Glyceryl monostearate SE	0.9
Sorbitan stearate	Sorbitan stearate	1.5
Stearyl alcohol	Stearyl alcohol	0.5

Phase C

Iron oxide	2.0
Titanium dioxide	6.0
Kaolin	7.0

Phase D

DC 345	Cyclomethicone	15.0
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Phase E

Preservative	q.s.
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Mixing Procedure: Phase A and phase B were combined separately and heated to 75°C.

Phase B was added to A with good mixing. The mixture was cooled with continued mixing

- 5 to 60°C and added phase C, then phase D was added. The mixture was mixed and cooled to less than 40°C. Phase E was added and then homogenized for 1-2 minutes.

In this face foundation, or any other color cosmetic products, Dermacryl AQF offers extended wear, crease resistance, and water resistance.

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Example 11 – Skin Moisturizer

Ingredient	INCI name	%w/w
Phase A		Formula 12
Tegin M	Glycerin monostearate	0.95
Stearic acid	Stearic acid	1.9
Finsolv TN	C12-15 Alkyl Benzoate	2.5
Miglycol 812	Caprylic/Capric Triglyceride	3.0
Isopropyl Myristate	Isopropyl Myristate	2.5
Jojoba oil	Jojoba oil	2.0
Phase B		
Deionized water		q.s.
TEA 99%	Triethanolamine	0.35
Glycerin	Glycerin	3.0
Xanthan gum		0.6
Phase C		
Dermacryl AQF (45% active) polymer	Acrylates copolymer	4.40
Phase D		
Preservative		q.s.

- 5 a) Mixing procedure: Phase A was combined and heated to 75°C. Phase B and Dermacryl AQF were mixed to ensure that the xanthan gum was fully dispersed, then heated to 75°C. Phase A was added to B with good mixing. The mixture was cooled with continued mixing to below 40°C, phases C and D were then added.
- b) The mixing procedure of (a) was repeated except that Dermacryl AQF was added at 75°C after combining phase A and B.
- 10 In this formula, Dermacryl AQF polymer acts as a film former to provide moisture protection or moisturization by maintaining occlusivity, in addition to extending the wear (including water resistance) of the product.